

Electrochemical Studies on 2- & 3-Mercaptopropionic Acids

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Electrochemical behaviour of 2- and 3-mercaptopropionic acids has been studied at dropping mercury and rotating platinum electrodes. Well-defined S-shaped single waves are obtained for the oxidation of these compounds at d.m.e. in solutions containing buffers of $pH > 6$. The anodic wave for either of these compounds is, however, associated with a pre-wave at $pH < 6$. The pre-wave tends to merge with the main wave with increase in pH . The oxidation at platinum electrode takes place at more positive potentials and the product of oxidation is a disulphide, unlike a mercaptide at d.m.e.

THE polarographic behaviour of 2-mercaptopropionic acid¹ (2-MPA) and 3-mercaptopropionic acid² (3-MPA) has been studied at d.m.e. in Clark and Lub's buffers of different pH values. The wave height of 3-MPA has been reported to decrease gradually in solutions of $pH > 5.8$ till the wave vanishes at $pH > 7.90$. This behaviour has been attributed to the formation of a film of mercury compound of 3-MPA around the drop, preventing further interaction of the depolarizer and the mercury drop². No such behaviour has been reported for 2-MPA¹. The present studies were, therefore, undertaken mainly to investigate this difference in behaviour of the two closely related compounds. Since d.m.e. is not an indifferent electrode for these compounds, their electrochemical behaviour at rotating platinum electrode has also been studied.

Materials and Methods

2- and 3-mercaptopropionic acids (Koch-Light, England), potassium nitrate, sodium hydroxide (BDH, AnalaR) and perchloric acid (Riedel) were used as such. All the solutions were prepared in air-free conductivity water. Fresh solutions of 2-MPA and 3-MPA for each polarographic were used every day and were standardized as reported earlier³. Double strength Britton-Robinson (BR) buffers of different pH values were used.

Polarograms were recorded at $25 \pm 0.5^\circ$ and at different temperatures on a Sargent-Welch polarograph model XVI using a thermostated H-type cell. An iR compensator⁴ in conjunction with three electrode cell was used while working with ethanolic solutions. The pH measurements were made on ELICO pH meter model L1-10 using glass and calomel electrodes. The capillary characteristics measured in 0.1M potassium nitrate at $E_{1.e.} = 0.4$ (vs SCE) and at a mercury height of 66.0 cm were: $m = 1.993$ mg sec⁻¹; $t = 4.40$ sec; and $m^{2/3}t^{1/6} = 2.027$ mg^{2/3} sec^{-1/2}.

Purified nitrogen presaturated with the background solution to be polarographed was used for deaeration and an inert atmosphere was maintained over the solution during electrolysis. Gelatin (0.5%) was

used as maxima suppressor. Necessary corrections were made in processing the diffusion current data.

Voltammetric oxidations were carried out at rotating platinum electrode (600 rpm) in a buffer of pH 9.0 containing 0.1M KNO₃. Complete electrolysis of 10⁻³M solutions of 2-MPA and 3-MPA at pH 9.0 was carried out at controlled potential at a large platinum electrode exposed to a potential of 0.8 V (vs SCE) and the polarograms of the resulting solutions were recorded.

Results and Discussion

The polarograms of 2-MPA and 3-MPA (10⁻³M) in 0.1M perchloric acid, 0.1M sodium hydroxide and BR buffers of different pH values (all containing 0.1M potassium nitrate) are shown in Fig. 1 (A and B). Whereas Saxena and coworkers^{1,2} have reported a single reversible anodic wave for 2-MPA and 3-MPA corresponding to the formation of the respective mercaptides, a distinct pre-wave associated with the main wave (at $pH < 6.0$) is observed in the present studies probably due to more sensitive instrumentation. The occurrence of pre-wave has been reported earlier for a number of sulphhydryl compounds and attributed to the tendency of the reaction product to get adsorbed on the drop surface⁵. In the present studies, the two waves are best distinct in 0.1M perchloric acid and in buffer of pH 2.0. The difference in half-wave potentials of these waves gradually decreases with the increase in pH . The pre-wave merges in the main wave giving a single well-defined S-shaped wave in buffers of $pH > 6.0$.

The behaviour of 3-MPA is similar to that exhibited by 2-MPA even in higher pH buffers and no irregular decrease in diffusion current with pH is found as reported earlier by Saxena and Gupta². However, a slight decrease in the limiting current in highly alkaline solutions is observed in the present studies as well. It may be attributed to the air-oxidation of mercaptopropionic acids under the experimental conditions during the various operations as suggested by Reid⁶.

Effect of varying 2-MPA and 3-MPA concentrations on pre-wave — The polarograms of the solutions of

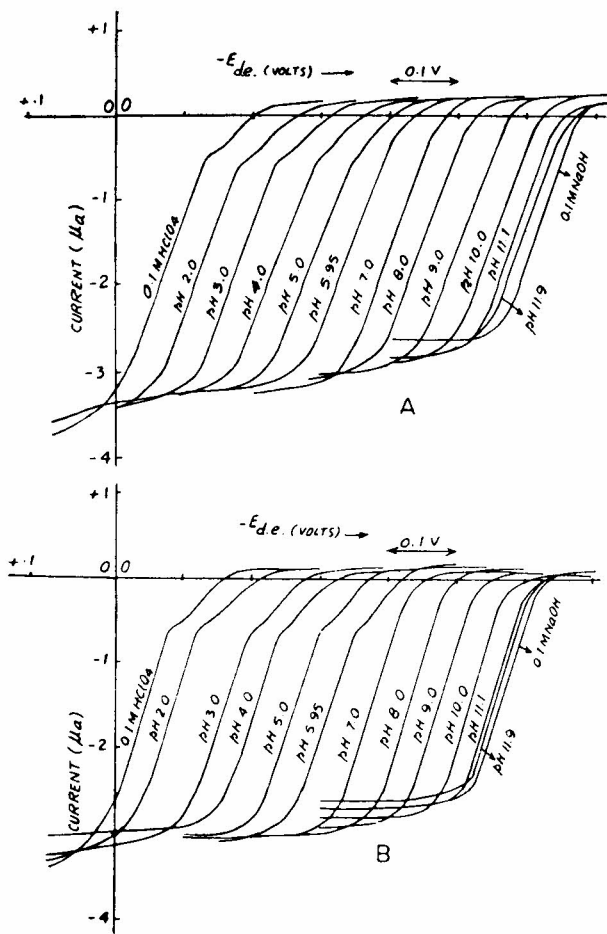


Fig. 1—Polarograms of (A) 2-mercaptopropionic acid ($10^{-3}M$) and (B) 3-mercaptopropionic acid ($10^{-3}M$) at different pH values

different concentrations of 2-MPA and 3-MPA ($0.05-2.0 \times 10^{-3}M$) are recorded at different pH values. Some typical results are presented in Table 1. In solutions containing buffers of pH < 6,

TABLE 1—EFFECT OF VARYING [2-MPA] AND [3-MPA] ON THE WAVE HEIGHTS IN A BUFFER OF pH 2.0

Conc. (C) mM	Pre-wave height (i_a) (µa)	i_a/C	Total wave height (i_d) (µa)	i_d/C
2-MPA				
0.05	0.18	3.60	0.18	3.60
0.10	0.34	3.40	0.34	3.40
0.20	0.69	3.45	0.69	3.45
0.40	0.68	1.70	1.37	3.43
0.60	0.68	1.13	2.03	3.38
1.00	0.68	0.68	3.38	3.38
2.00	0.68	0.34	6.76	3.38
3-MPA				
0.05	0.16	3.20	0.16	3.200
0.10	0.32	3.20	0.32	3.200
0.20	0.63	3.15	0.63	3.150
0.40	0.70	1.75	1.26	3.150
0.60	0.70	1.17	1.88	3.133
1.00	0.70	0.70	3.14	3.140
2.00	0.70	0.35	6.27	3.135

only a pre-wave is observed if the concentration of 2-MPA or 3-MPA is $< 2.0 \times 10^{-4}M$. Under these conditions, the height of the pre-wave is a direct function of [depolarizer]. At concentrations $> 2.0 \times 10^{-4}M$, the main anodic wave starts forming in addition to the pre-wave if the solutions contain buffers of pH < 6. Any further increase in [depolarizer] increases the height of only the main wave indicating, thereby, the adsorption nature of the pre-wave. The sum of the pre-wave and main wave heights is, however, proportional to the concentration. Half-wave potentials of the pre-wave and the main wave are independent of [depolarizer].

Only the main anodic wave is observed in solutions containing buffers of pH > 6. The height of the anodic wave is proportional to [depolarizer] whereas the $E_{1/2}$ remains independent of its concentration.

Effect of mercury height and temperature on the pre-wave—The effect of the mercury height (h) on the wave height (s) has been studied in all the solutions. Some typical results are presented in Table 2. If a pre-wave is observed along with the main wave, the sum of the heights of these waves is a function of $\sqrt{h_{eff}}$ indicating the diffusion-controlled nature of the anodic reaction. The limiting height of the pre-wave alone is, however, proportional to h_{eff} showing the adsorption nature of the pre-wave⁷. In case there is no pre-wave, the height of the main wave is proportional to $\sqrt{h_{eff}}$ showing its diffusion-controlled nature.

The magnitude of the difference in $E_{1/2}$ of the pre-wave and the main wave decreases with increase in temperature and only a single wave is observed at temperatures above 40°. It lends further support to the adsorption nature of the pre-wave since the adsorption energy decreases with increase in temperature.

TABLE 2—EFFECT OF DROP TIME ON WAVE HEIGHTS OF 2- AND 3-MERCAPTOPROPIONIC ACIDS ($10^{-3}M$)

[$h_{soln} = 3.0$ cm (= 0.220 cm of Hg); back pressure = $\frac{3.1}{(1.993 \times 4.40)^{1/3}} = 1.503$]

h_{Hg} (cm)	h_{eff} (cm)	Limiting pre-wave height (i_a) (µa)	$\frac{i_a}{h_{eff}}$	Total wave height (i_d) µa	$\frac{i_d}{\sqrt{h_{eff}}}$
2-MPA; pH = 3.0					
50	48.277	0.45	0.0093	2.66	0.3828
60	58.277	0.54	0.0093	3.05	0.3997
70	68.277	0.63	0.0093	3.27	0.3954
75	73.277	0.68	0.0093	3.38	0.3950
80	78.277	0.73	0.0093	3.52	0.3971
85	83.277	0.77	0.0093	3.63	0.3980
3-MPA; pH = 2.0					
50	48.277	0.46	0.0095	2.55	0.3670
60	58.277	0.56	0.0096	2.82	0.3696
70	68.277	0.65	0.0095	3.02	0.3655
75	73.277	0.70	0.0096	3.14	0.3668
80	78.277	0.76	0.0097	3.24	0.3665
85	83.277	0.80	0.0096	3.35	0.3673

Effect of ethanol concentration — Keeping in view the adsorption nature of the pre-wave, it is considered worth while to study the effect of ethanol concentration on it. Polarograms of both the compounds when recorded in solutions containing varying concentrations of ethanol in 0.1M perchloric acid show that the pre-wave tends to merge with the main wave with the increase in ethanol concentration and only one wave is observed in solutions containing more than 50% ethanol. This supplements the adsorption nature of the wave and indicates that the tendency of the reaction product of these compounds at d.m.e. to get adsorbed on to the mercury drop decreases with the increasing ethanol concentration. The total limiting diffusion current decreases with increase in ethanol concentration and becomes practically constant when the solution contains 40% or more of ethanol. The $E_{1/2}$ of the single wave obtained in solution containing more than 50% ethanol is independent of ethanol concentration.

Determination of dissociation constant — The dissociation constant of 2-MPA has been reported to be 10.40 (ref. 1). However, the dissociation constant of 3-MPA has not been determined by SAXENA and Gupta², due to irregular waves obtained at higher pH values. Since regular waves are obtained in the present studies, the dissociation constant of 3-MPA is determined for comparison. Fig. 2 shows that the plot of pH vs $E_{1/2}$ of anodic waves of 3-MPA ($10^{-3}M$)

obtained from the plots of $E_{d.e.}$ vs $\log \frac{i_a - i}{i}$ has two linear portions intersecting at a point corresponding to pH 10.4. The pK value of the sulphhydryl group in 3-MPA is, therefore, 10.4 under the experimental conditions. Below this pH, the slope of the curve is 0.0595 V as compared with the theoretical value of 0.059 V for one electron process at 25°, suggesting thereby that only one H^+ takes part in the electrode reaction. Since there is no increase in $E_{1/2}$ above pH 10.4, there is no replacement of H^+ beyond this pH.

Anodic oxidation at platinum electrode — Voltammograms of 2-MPA and 3-MPA in BR buffer of pH 9.0 (containing 0.1M KNO_3) at rotating platinum electrode are recorded to compare the behavior at rotating platinum electrode and d.m.e. The waves at rotating platinum electrode are well defined with $E_{1/2}$ of 0.460 V and 0.465 V respectively.

The same solutions after electrolysis at a large platinum electrode for 4 hr at potential of +0.8 V (vs SCE) give irreversible cathodic waves at d.m.e. at more negative reduction potentials with

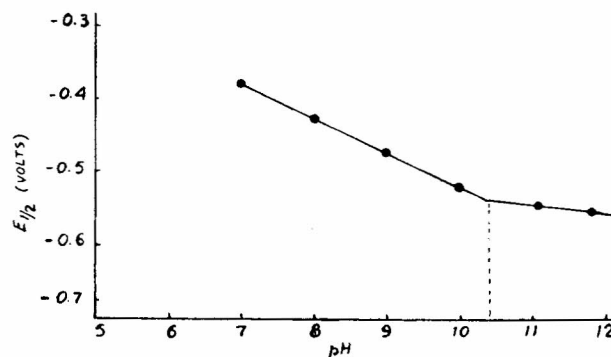


Fig. 2 — Plot of $E_{1/2}$ of 3-mercaptopropionic acid as a function of pH

$E_{1/2}$ of -0.950 V and -0.960 V respectively. These solutions on further addition of MPA (0.1M) give two distinct waves in each case indicating, thereby, the irreversible nature of the oxidation reaction at the platinum electrode.

The mercaptans are known to form respective disulphides on air oxidation, more so in alkaline solution⁶. Purified air was, therefore, passed through the solutions of 2- and 3-mercaptopropionic acids for over 10 hr and the polarograms of the resulting solutions recorded. The product of the air oxidation showed the waves with the same $E_{1/2}$ values as those of the oxidation product at a large platinum electrode. It may thus be concluded that the oxidation product at the platinum electrode is the corresponding disulphide, whereas the mercaptide is formed during the electrolysis at d.m.e.^{1,2}.

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